METHOD 3015

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA), graphite furnace absorption spectroscopy (GFAA), inductively coupled argon plasma spectroscopy (ICP), or inductively coupled argon plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3015.

1.2 Samples prepared by Method 3015 using nitric acid digestion may be analyzed by FLAA, GFAA, ICP-AES, or ICP-MS for the following:

Aluminum	Lead
Antimony	Magnesium
Arsenic*	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	Selenium*
Chromium	Silver
Cobalt	Sodium
Copper	Thallium
Iron	Vanadium
	Zinc

*Cannot be analyzed by FLAA

2.0 SUMMARY OF METHOD

2.1 A representative 45 mL aqueous sample is digested in 5 mL of concentrated nitric acid in a fluorocarbon (PFA or TFM) digestion vessel for 20 minutes using microwave heating. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle in a clean sample bottle prior to analysis.

3.0 INTERFERENCES

3.1 Many samples that contain organics, such as TCLP extracts, will result in higher vessel pressures which have the potential to cause venting of the vessels. Venting can result in either loss of analytes and/or sample, which

must be avoided. A smaller sample size can be used but the final water volume prior to nitric acid addition must remain at 45 mL. This is required to retain the heat characteristics of the calibration procedure. Limits of quantitation will change with sample quantity (dilution) as with instrumentation."

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements

4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Temperature monitoring and control of the microwave unit are desirable.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psig) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psig).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several significant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vessels equipped with venting features, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.

CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the oven under certain pressures. Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mechanisms or containers with fluorocarbon (PFA or TFM) liners and pressure relief mechanisms are considered acceptable at present.

Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief valves for microwave acid digestions by this method. Use of laboratory grade microwave equipment is required to prevent safety hazards. For further information consult reference 1.

CAUTION: In addition, there are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Analytical balance, 300 g capacity, minimum accuracy ± 0.01 g.

4.5 Filter funnel, glass or disposable polypropylene.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 2).

5.3 Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurities. If the method blank is less than the MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic containers are preferable. See Chapter Three, Step 3.1.3 of this manual, for further information.

6.3 Aqueous waste waters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100,99,98,97, 95,90,80,70,60,50, and 40% using the procedure described in section 7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.1.4, and calculate the power setting corresponding to the required power in watts specified in the procedure from the (2-point) line. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2 °C). One kg of reagent water is weighed (1,000.0 g $\pm$ 0.1 g) into a fluorocarbon (PFA or TFM) beaker or a beaker made of some other

material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2 °C measured to ± 0.05 °C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05 °C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2 °C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship

$$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t} \qquad \text{Eq. 1}$$

Where:

P = the apparent power absorbed by the sample in watts (W). (W=joule·sec^{-1})

K = the conversion factor for thermochemical calories·sec^{-1} to watts (=4.184)

C_p = the heat capacity, thermal capacity, or specific heat (cal·g^{-1}·$°C^{-1}$), of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g^{-1}·$°C^{-1}$) the calibration equation simplifies to:

$$P = (\Delta T)\ (34.86)$$

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration power. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high solids (concentrated) samples and low solids (low concentration) samples all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours, rinsed with reagent water, and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. In addition, to avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and cap assembly to 0.01 g prior to use.

7.3.2 A 45 mL aliquot of a well shaken sample is measured in a graduated cylinder. This aliquot is poured into the digestion vessel with the number of the vessel recorded on the preparation sheet.

7.3.3 A blank sample of reagent water is treated in the same manner along with spikes and duplicates.

7.3.4 Add 5 mL of concentrated nitric acid to each vessel that will be used. Check to make sure the pressure relief disks are in the caps with the smooth side toward the sample and start the caps a few turns on the vessels. Finish tightening the caps in the capping station which will tighten them to a uniform torque pressure of 12 ft-lbs. (16 N-m) or to the manufacturers recommended specifications. Weigh each capped vessel to the nearest 0.01 g.

CAUTION: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

7.3.5 Evenly distributed the vessels in the carousel according to the manufacturer's recommended specifications. Blanks are treated

as samples for the purpose of balancing the power input. When fewer than the recommended number of samples are digested, the remaining vessels should be filled with 45 mL of reagent water and 5 mL of nitric acid to achieve the full compliment of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 1).

7.3.6 Program the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes. The chosen sequence will bring the samples to 160°C ± 4°C in 10 minutes and will permit a slow rise to 165-170 °C during the second 10 minutes (Ref. 3). Start the turntable motor and be sure the vent fan is running on high and the turntable is turning. Start the microwave generator.

7.3.6.1 Newer microwave units are capable of higher power that permit digestion of a larger number of samples per batch. If the analyst wishes to digest more samples at a time, the analyst may use different power settings as long as they result in the same time and temperature conditions defined in 7.3.6. That is, any sequence of power that brings the samples to 160°C ± 4°C in 10 minutes and permits a slow rise to 165-170°C during the second 10 minutes (Ref. 2).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings are provided to reproduce the reaction conditions defined in 7.3.6, then these alternative vessels may be used (Ref. 1,3)

7.3.7 At the end of the microwave program, allow the vessels to cool for at least 5 minutes in the unit before removal to avoid possible injury if a vessel vents immediately after microwave heating. The samples may be cooled outside the unit by removing the carousel and allowing the samples to cool on the bench or in a water bath. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of the sample plus acid has decreased by more than 10% discard the sample.

7.3.8 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle or filtered.

7.3.8.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.8.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.8.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned cotainer.

7.3.9 The concentration values obtained from analysis must be corrected for the dilution factor from the acid addition. If the sample will be analyzed by ICP-MS additional dilution will generally be necessary. For example, the sample may be diluted by a factor of 20 with reagent water and the acid strength adjusted back to 10% prior to analysis. The dilutions used should be recorded and the measured concentrations adjusted accordingly (e.g., for a 45 mL sample and 5 mL of acid the correction factor is 1.11).

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One, of this Manual, should be followed.

8.2 For each analytical batch of samples processed, analytical reagent blanks (also field blanks if they were taken) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.3 Duplicate samples should be processed on a routine basis. A duplicate sample is a real sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Refer to Table 1 for a summary of performance data.

10.0 REFERENCES

1. Introduction to Microwave Sample Preparation: Theory and Practice, Kingston, H. M.; Jassie, L. B., Eds.; ACS Professional Reference Book Series: American Chemical Society, Washington, DC, 1988; Ch 6 & 11.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Kingston, H. M., Final Report EPA IAG #DWI3932541-01-I, September 30, 1988, Appendix A.

4. Shannon, M., Alternate Test Procedure Application, USEPA Region V, Central Regional Laboratory, 536 S. Clark Street, Chicago, IL 60606, 1989.

5. Kingston, H. M., Walter, P. J., "Comparison of Microwave Versus Conventional Dissolution for Environmental Applications", Spectroscopy, vol. 7 No. 9,20-27,1992.

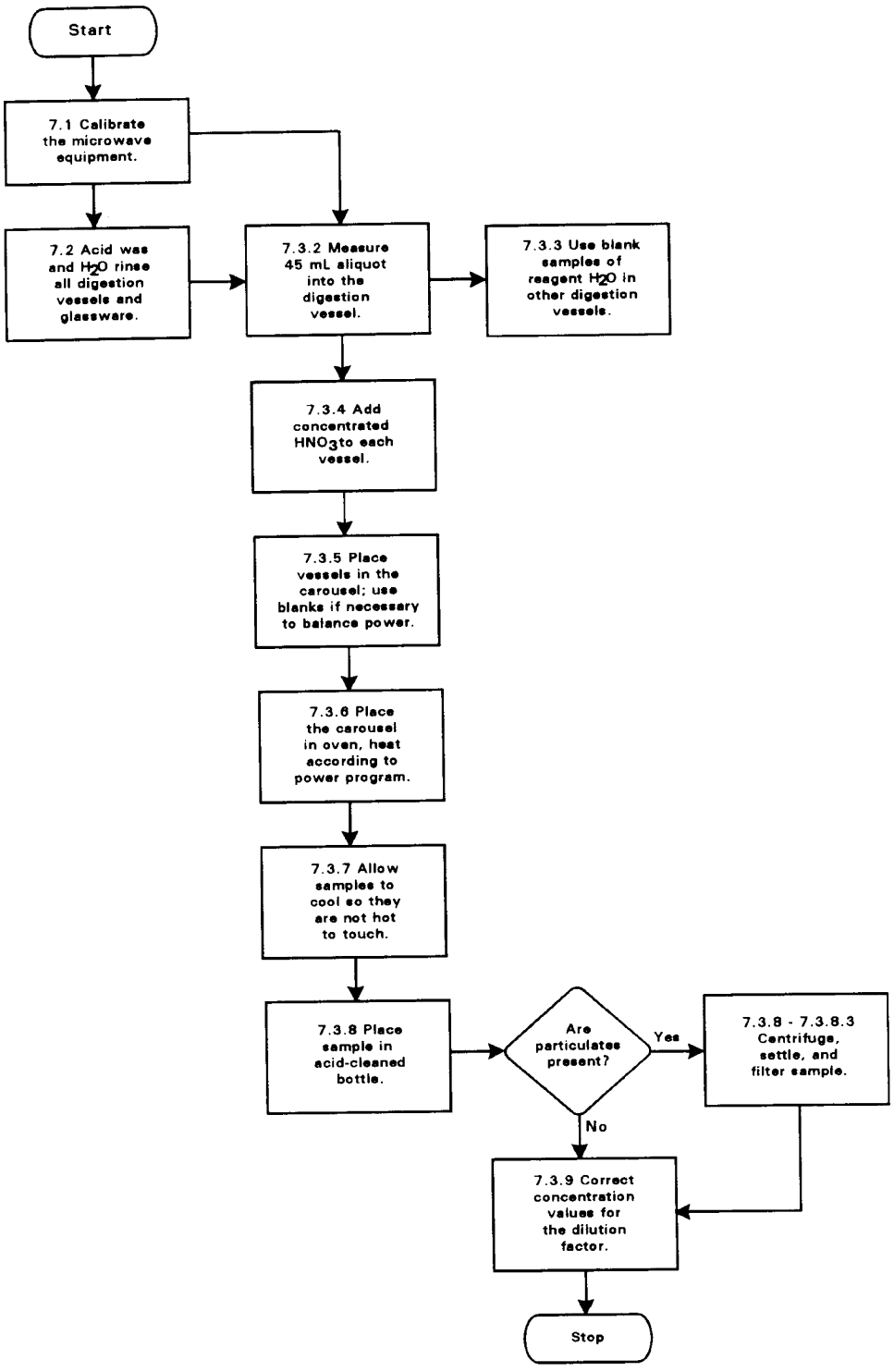
6. Sosinski, P., and Sze C., "Absolute Accuracy Study, Microwave Digestion Method 3015 (Nitric acid only)"; EPA Region III Central Regional Laboratory, 1991.

TABLE 1
MICROWAVE DIGESTION METHOD 3015 (Nitric Acid Only)

Elem	Material	Certified Mean	Observed Mean	Std. Dev.	Relative Standard Deviation	Relative Bias
Al	Tm-11	510.0	485.5	26.3	5.4	-4.80%
Al	Tm-12	2687.0	2770.6	88.2	3.2	3.11%
Al	T-107	220.0	213.5	19.3	9.0	-2.95%
Al	T-109	113.0	117.7	30.6	2.6	4.16%
Ba	Tm-11	450.0	441.4	23.4	5.3	-1.90%
Ba	Tm-12	2529.0	2431.4	70.3	2.9	-3.86%
Ba	T-107	192.0	196.6	15.9	8.1	2.44%
Cd	Tm-11	40.8	44.6	2.1	4.7	9.46%
Cd	Tm-12	237.0	242.3	8	3.3	2.25%
Cd	T-107	14.3	12.4	0.9	7.2	-12.94%
Cd	T-109	12.1	10.3	1.7	16.5	-14.55%
Zn	Tm-11	55.4	55.9	2.6	4.6	1.06%
Zn	Tm-12	314.0	316.5	8.9	2.8	0.82%
Zn	T-107	75.8	81.6	3.3	4.0	7.68%
Zn	T-109	74.0	69.9	4.1	5.8	-5.46%
As	T-107	10.8	12.8	0.84	6.5	19.26%
As	T-109	8.15	90.6	11.0	12.2	11.26%
Co	Tm-11	227.0	242.6	14.1	5.8	6.90%
Co	Tm-12	1067.0	1153.3	35.9	3.1	8.09%
K	T-95	4700.0	5080.3	784	15.4	8.09%
K	T-109	2330.0	2601.5	383.4	14.7	11.65%
Ni	Tm-11	264.0	284.3	16.5	5.8	7.71%
Ni	Tm-12	1234.0	1293.0	39.4	3.0	4.79%
Ni	T-109	57.0	60.8	3.09	5.0	6.72%
Pb	Tm-11	275.0	275.9	32.2	11.7	0.36%
Pb	Tm-12	1326.0	1359.0	35.0	2.6	2.49%
Pb	T-107	26.0	30.0	0.2	0.66	15.65%
Pb	T-109	34.9	39.3	1.2	3.0	12.69%
Sb	WP980-1	16.9	18.3	0.47	2.6	8.27%
Sb	WP980-2	101.5	108.9	34.4	31.6	7.33%
Se	T-95	60.1	65.9	2.6	3.94	9.77%
Se	T-107	11.0	13.0	0.9	6.9	19.00%
Tl	WP980-1	50.0	55.1	2	3.6	10.26%
Tl	WP980-2	6.3	7.0	0.52	7.4	11.66%
V	Tm-11	491.0	532.6	26.1	4.9	8.48%
V	Tm-12	2319.0	2412.8	60.6	2.5	4.05%
Be	T-107	11.0	11.3	0.53	4.7	3.00%
Be	T-109	22.1	25.6	0.91	3.6	15.97%
Ca	T-107	11700.0	12364.0	783.6	6.3	5.68%
Ca	T-109	35400.0	38885.0	999	2.6	9.84%

TABLE 1 (continued)

Elem	Material	Certified Mean	Observed Mean	Std. Dev.	Relative Standard Deviation	Relative Bias
Mg	T-95	32800.0	35002.0	1900	5.4	6.71%
Mg	T-107	2100.0	2246.7	110.5	4.9	6.99%
Mg	T-109	9310.0	10221.7	218.6	2.1	9.79%
Na	T-95	190000.0	218130.0	10700	4.9	14.81%
Na	T-107	20700.0	22528.0	1060	4.7	8.83%
Na	T-109	12000.0	13799.5	516.2	3.7	15.00%
Cr	Tm-11	52.1	64.3	4.1	6.4	23.51%
Cr	Tm-12	299.0	346.0	9.8	2.8	15.74%
Cr	T-107	13.0	22.3	1.5	6.7	71.77%
Cr	T-109	18.7	32.6	6.4	19.6	74.71%
Cu	Tm-11	46.3	76.5	4.4	5.7	65.36%
Cu	Tm-12	288.0	324.0	8.9	2.7	12.52%
Cu	T-107	30.0	42.3	4.0	9.4	41.17%
Cu	T-109	21.4	54.0	3.6	6.7	152.38%
Fe	Tm-11	249.0	289.3	16.4	5.7	16.18%
Fe	Tm-12	1089.0	1182.5	43.5	3.7	8.59%
Fe	T-107	52.0	63.8	8.7	13.6	22.69%
Fe	T-109	106.0	134.0	6.6	4.9	26.50%
Mn	Tm-11	46.0	60.9	3.2	5.2	32.48%
Mn	Tm-12	263.0	304.4	9.1	3.0	15.77%
Mn	T-107	45.0	52.6	3.1	5.9	17.09%
Mn	T-109	34.0	46.6	3.0	6.4	37.18%
Ag	WS378-1	46.0	19.4	5.6	2.9	-57.83%


Start
7.1 Calibrate the microwave equipment.
7.2 Acid was and H_2O rinse all digestion vessels and glassware.
7.3.2 Measure 45 mL aliquot into the digestion vessel.
7.3.3 Use blank samples of reagent H_2O in other digestion vessels.
7.3.4 Add concentrated HNO_3 to each vessel.
7.3.5 Place vessels in the carousel; use blanks if necessary to balance power.
7.3.6 Place the carousel in oven, heat according to power program.
7.3.7 Allow samples to cool so they are not hot to touch.
7.3.8 Place sample in acid-cleaned bottle.
Are particulates present?
Yes
7.3.8 - 7.3.8.3 Centrifuge, settle, and filter sample.
No
7.3.9 Correct concentration values for the dilution factor.
Stop